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Bauhinia racemosa sawdust as an novel biosorbent for hexavalent chromium removal with optimization and mechanistic insight

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Abstract

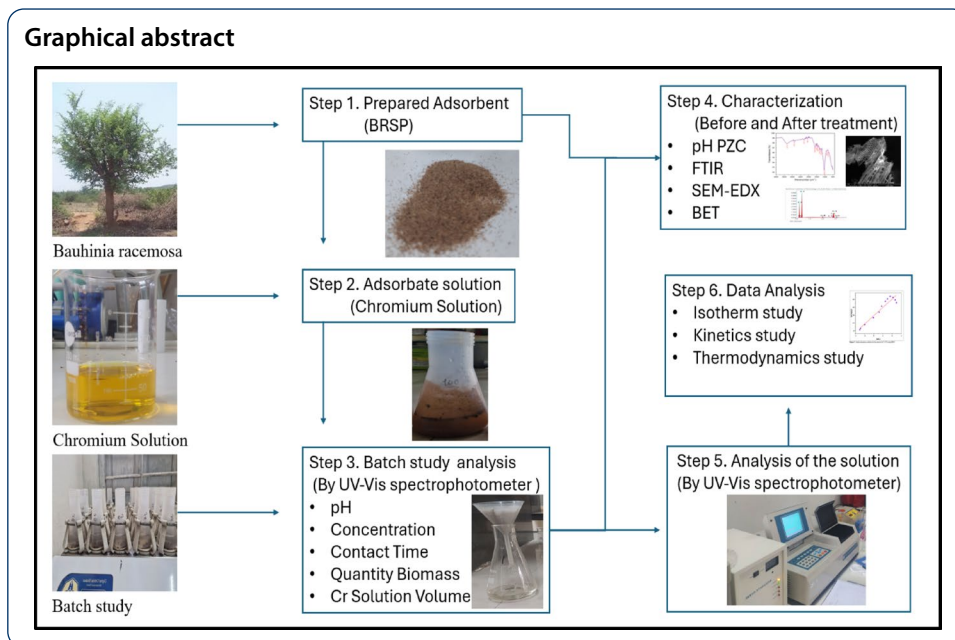
Present study evaluates *Bauhinia racemosa* sawdust powder (BRSP) an underutilized agro waste as a sustainable, low-cost biosorbent for hexavalent chromium [Cr(VI)] removal from aqueous solutions. Systematic batch adsorption experiments revealed a peak Cr(VI) removal of 99.78% and an adsorption capacity of 106.86 mg g⁻¹ under optimized conditions (pH 4.0, 0.5 g/100 mL dosage, particle size 75 μm, 100 mg L⁻¹ initial concentration, and 60 min contact time). Comprehensive physiochemical characterization confirmed its suitability: BET analysis revealed a specific surface area of 212.2 m²g⁻¹, pore volume of 0.323 cm³g⁻¹, and mesoporous structure (average pore diameter of 6.4 nm). Boehm titration and pHPZC (2.7) showed abundant acidic groups while FTIR spectroscopy confirmed the involvement of hydroxyl, carboxyl, and amine groups. SEM-EDX analyses revealed morphological changes and chromium deposition (~0.6 wt%) post adsorption. Adsorption equilibrium data fitted best to the Langmuir model (q_{max} = 106.86 mg g⁻¹, R² = 0.991), with kinetics following a pseudo-second-order model (R² = 0.999), and thermodynamic analysis (ΔG° = - 8.1 to - 10.5 kJ mol⁻¹; ΔH° = +22.6 kJ mol⁻¹) indicating a spontaneous, endothermic process. *Bauhinia racemosa* sawdust, an underexplored lignocellulosic biomass, exhibited superior performance compared to previously reported agro-waste biosorbents, highlighting its novelty and potential. This study positions BRSP as a promising and sustainable material for efficient Cr(VI) remediation contributing to the progression of green technologies in wastewater treatment.

Highlights

- *Bauhinia Racemosa* sawdust powder (BRSP) demonstrates excellent biosorption of Cr(VI).
- FTIR, BET, and SEM-EDX analyses were performed for surface studies.
- The adsorption data fitted well to the Freundlich, Langmuir, Temkin, and D-R isotherms, whereas the kinetics adhered to a pseudo-first-order kinetic model.
- Thermodynamic investigations showed that the adsorption process was endothermic and spontaneous at ambient temperature.
- BRSP demonstrated a significant adsorption capability of 106.86 mg/g at an optimum pH of 4.0.

Keywords Adsorption, Hexavalent chromium, Isotherm models, BET, SEM-EDX





1 Introduction

Recent decade witnessed rapid industrialization which has intensified the release of noxious heavy metals into aquatic ecosystems, with hexavalent chromium [Cr(VI)] being among the most perilous. Recognized for its high solubility, mobility, and persistence, Cr(VI) is classified as a carcinogenic and mutagenic contaminant associated with respiratory disorders, renal dysfunction, and genetic mutations [1–5]. To safeguard human and environmental health, the World Health Organization (WHO) has established a stringent permissible limit of ≤ 0.05 mg/L of total chromium in drinking water [4, 5]. In alignment with these standards, several legislation frameworks (Table 1) have backed the importance of developing effective Cr(VI) mitigation technologies.

Traditional treatment techniques- comprising chemical precipitation, electrocoagulation, ion exchange, membrane filtration, and photoreduction have been practiced for Cr(VI) removal [6–9]. While operative under specific conditions, these processes often encounter constraints such as high operative and maintenance costs, generation of secondary pollutants, and limited application at low metal ion concentrations. These challenges underline the necessity for sustainable, cost-effective, and environmentally benign substitutes [10].

Adsorption has originated as a superior alternative by virtue of operational easiness, scalability, and efficiency even at a trace level of metal ion concentrations. Low-priced biosorbents resulting from agrarian and industrial remnant have grabbed attention, allying with values of circular economy and waste valorization [11]. Nevertheless, the practical deployment of adsorption process is limited by adsorbent regeneration, reduced performance upon repeated usage, and challenges in sizable implementation. Addressing this void requires systematic exploration of abundant, renewable biomaterials with favourable surface chemistry for Cr(VI) sequestration.

Sawdust distinct out among lignocellulosic by-products due to its opulence, low price, and minimalist environmental impact [12, 13]. Globally, sawmills produce millions of tonnes yearly, with India contributing 18.91 million tonnes from over 23,000 sawmills

Table 1 Regulatory limits of cr(VI) and cr(III) in drinking water in major countries

Authority/Country	Cr(VI) limit (mg/L)	Cr (III) limit (mg/L)	Total Cr (mg/L)	Ref-er-ence
World Health Organization (WHO)	0.05	NS	–	[25]
Bureau of India Standards (BIS)	0.05	NS	–	[26]
India Central Pollution control Board (CPCB)	0.1	2.0	2.0	[27]
United States (USEPA)	0.01 (as total Cr)	–	0.1	[28]
European Union (EU)	0.05 (as total Cr)	–	0.05	[29]
Canada (Health Canada)	0.05	NS	–	[30]
Australia (ADWG)	0.05 (as total Cr)	–	0.05	[31]
South Africa (SANS 241)	0.05	NS	–	[32]
Japan (JWWA)	0.05	NS	–	[33]
Malaysia (MOH)	0.05 (as total Cr)	–	0.05	[34]
Germany (UBA)	0.05	NS	–	[35]

NS: Not specified

[14, 15]. Owing to its porous nature and compositional value of cellulose, hemicellulose, and lignin, sawdust displays varied functional groups exhibiting binding heavy metals on their surface [16]. Earlier studies have secured its potential for adsorbing Pb, Cd, Cu, and Zn, yet methodical analysis on its Cr(VI) removal adequacy, particularly employing species-specific sawdust, remain limited [16, 17]. In the present study, *B. racemosa* sawdust was explored for its Cr(VI) removal potential. Batch adsorption research was employed to optimize the following operating parameters: the volume of the Cr solution, the pH of the adsorbate, the amount of biosorbent, the starting concentration of the adsorbate, the contact time, and the size of the biosorbent's particles. Furthermore, the adsorption process has been elucidated by the use of thermodynamic studies, various kinetic models, and adsorption isotherms [18].

Equilibrium adsorption data were analysed using four different isotherm models: Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich (D-R). Freundlich model elucidates multilayer adsorption on heterogeneous surfaces whereas the Langmuir model illustrates monolayer adsorption on a homogeneous surface [19]. Adsorbate-adsorbent interactions were studied by Temkin isotherm, while Dubinin-Radushkevich model presents insights into adsorption energy [20–22].

Thermodynamic parameters like Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were computed to determine the spontaneity and feasibility of the method [23, 24]. To find the rate and mechanism of adsorption, Kinetic behaviour was checked using pseudo-first-order and pseudo-second-order models. The physicochemical characterization of BRSP was accomplished using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), Boehm titration, and proximate analysis. FTIR study ascertained functional groups participating in Cr(VI) uptake, SEM-EDX reported morphological and elemental features, and Boehm titration assessed surface functional groups.

This study envisaged producing a cost-effective and environmentally sustainable biosorbent, *B. racemosa* sawdust powder (BRSP), to sequester hazardous Cr(VI) from industrial effluents. It contributes to green policy for wastewater treatment, which is aligned with worldwide sustainability goals by valorizing agricultural waste through principles of green chemistry. Although numerous biosorbents such as rice husk, wheat straw, algal biomass, and fruit peels have been explored for Cr(VI) elimination, several suffer from

low adsorption capacities and high processing charges. BRSP, derived from unused biomass, suggests a favourable alternative. Advanced characterization and adsorption modeling affirm a high adsorption capacity (106.86 mg/g) and > 99% removal performance, approving chemisorption-based monolayer adsorption. These findings highlight BRSP's potential for scalable, sustainable waste management and environmental remediation.

2 Materials and methods

2.1 Preparation of biomaterial

The experiments were conducted using analytical-grade reagents (Merck, Germany) and borosilicate glassware, with all solutions prepared in distilled water. Cr(VI) Stock solution was obtained through the dissolution of 2.828 g of anhydrous potassium dichromate ($K_2Cr_2O_7$) into 1000 mL of distilled water. For the stabilization of stock solution, 1.5 mL of 1 M Nitric acid (HNO_3) was added to the aqueous medium [36]. Cr(VI) concentrations in aqueous samples and effluents were quantified using the 1,5-diphenylcarbazide (DPC) colorimetric method, in accordance with APHA standard protocols. Absorbance was measured at 540 nm using a UV-Visible spectrophotometer (Model CB-104, Chem Biotech, India). pH adjustments were made using HCl or NaOH and monitored via a digital pH meter (Model Eq. 618, Equitronics, India). A rotary shaker (Model B11-054, Biotechnics, India; ISO 9001:2008 certified) was used to conduct batch adsorption experiments at room temperature (25 ± 2 °C) at speeds ranging from 20 to 500 rpm. Proximate analysis of biosorbents was conducted using a hot air oven (Model BIT28, Bio-Tech) and a muffle furnace (Model BIT36, Bio-Tech), ensuring consistent thermal treatment and characterization of the adsorbent properties.

2.1.1 Biomass: source, collection, and processing

Plant Material (Source and Collection) Sawdust was provided by a sawmill near Udgaon, Maharashtra, India. It was packed in plastic bags and transported to the chemistry lab at Symbiosis Institute of Technology, Pune. The sawdust was sieved to remove large particles. It was thoroughly washed with distilled water to remove contaminants and dust. Post cleaning, the sawdust was left to dry in the sun for 1–2 days, followed by drying in an oven (Bio-technics India; BTI-29) at 150 °C for six hours per day over three days to remove excess moisture. Until a constant weight was obtained, the drying and cooling processes were performed multiple times. The sawdust was sieved to obtain a desired particle size of 75 μm and stored in an airtight container. The process for preparing the biosorbent is shown in Fig. 1.

2.1.2 Batch adsorption studies

Batch adsorption experiments were conducted in 250 mL Erlenmeyer flasks using a rotary shaker at 150 rpm and a controlled temperature of 25 ± 2 °C. To assess the impact of influencing factors i.e., effects of solution pH (1–12), contact time (5–200 min), adsorbent dosage (0.1–1.0 g), initial Cr(VI) concentration (5–300 mg L⁻¹), and solution volume (25–250 mL) were studied by changing one parameter and keeping others constant.

The solution pH was adjusted using standardized 1 M HNO_3 or NaOH solutions. The pH values were adjusted as needed for the experimental requirements. A preliminary study indicates a 60-minute time to attain adsorption equilibrium. Post adsorption, the

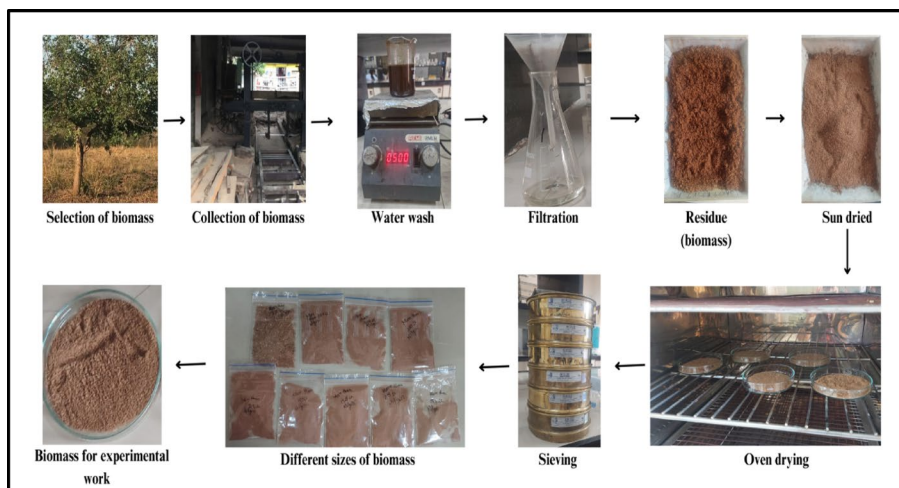


Fig. 1 Preparation of Biosorbent (BRSP) for Cr(VI) removal

suspensions were filtered through pre-washed Whatman No. 2 filter paper. Following APHA 2017 protocol, residual Cr(VI) concentration was checked using the DPC colour method at 540 nm with a UV-Vis spectrophotometer (Model CB-104, Chem Biotech, India).

This method follows the standard water testing procedures from APHA 2017. We performed the same experiment three times and reported the results as average values. Control experiments were conducted to check non-adsorptive losses further: (i) Cr(VI) solutions without BRSP and (ii) BRSP suspensions without Cr(VI). We calculated removal efficiency (%) and equilibrium adsorption capacity (q_e , mg g^{-1}) using the same standard equations to check how well the adsorption worked [37].

$$\text{Biosorption (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$Q = \frac{V (C_0 - C_e)}{m} \quad (2)$$

where

C_i = Cr(VI) solutions starting concentration (mg/L).

C_f = final concentration of Cr(VI) solution (mg/L).

V = solution volume (L).

C_0 = initial concentration of Cr(VI) solution (mg/L).

C_e = concentration of Cr(VI) solution at equilibrium (mg/L).

m = biomass quantity (g).

Q = metal uptake or adsorption ability (mg/g) [38, 39].

2.1.3 Elemental and compositional analysis of the BRSP

Proximate analysis of BRSP: Proximate analysis of sawdust was conducted following the guidelines established by the American Society for Testing and Materials (ASTM) standard [40, 41]. The moisture content (MC) was determined using the hot air oven-drying technique defined in the ASTM standard (D2867-09). A 1 g biomass sample was kept in a crucible and dried at 105 °C for three hours, post which it was cooled in a desiccator. A calibrated analytical balance (Wensar ISO 9001:2001, India) was used to weigh

the samples before and after drying. The moisture percentage in the biomass sample was calculated using Eq. 3 as follows:

$$MC (\%) = \left(\frac{B - C}{B - A} \right) \times 100 \quad (3)$$

Where, A = weight of empty crucible (g), B = weight of the crucible plus BRSP sample (g), C = weight of the empty crucible plus sample post drying and (MC) denotes the percentage of moisture content (%).

Volatile matter (VM) was determined using the ASTM standard (D5832-98) by placing a moisture-free biomass sample into a crucible and heating it for 7 min in a muffle furnace (Bio-Technics India BTI-2008) at 950 °C [42]. Cooled in desiccator and weighed using an electronic balance. The VM % was calculated by equation (Eq. no. 4):

$$VM (\%) = \left(\frac{D - B}{C - B} \right) \times 100 \quad (4)$$

where, VM represents the percentage of volatile matter in the biomass,

C = weight of crucible plus moisture-free sample (in grams), B refers to the weight of the empty crucible (g), and D = weight of the crucible plus ignited sample (g).

The ash content (AC) was determined according to ASTM standard (D2866-94): a 1 g BRSP sample was placed in a crucible and combusted for nearly half an hour at a temperature of 725 ± 25 °C in a muffle furnace. The samples were cooled in a desiccator and weighed using an electronic balance. AC was calculated using (Eq. No. 5):

$$AC (\%) = \left(\frac{D - B}{C - B} \right) \times 100 \quad (5)$$

Where B = weight of the crucible (g), C = weight of the crucible plus the initial biomass sample (g), and D = weight of the crucible and the ash sample (g) [43, 44].

To calculate Fixed carbon (FC) content Eq. 6 was used:

$$FC (\%) = 100 - [MC (\%) + VM (\%) + AC (\%)] \quad (6)$$

FC, MC, VM, and AC are the percentages of fixed carbon, moisture, volatile matter, and ash respectively .

Boehm titration of BRSP: To check the presence of functional group on biomaterial surfaces boehm titration was performed. It determines functional groups, including carboxyl, lactone, carbonyl, and basic groups. Sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate (NaHCO_3) are the three fundamental reagents selected to determine the acidic functional groups. To determine the number of basic functional groups hydrochloric acid (HCl) titration was performed [31, 45].

For experimentation, 0.1 g of sample was mixed with 50 ml each of 0.01 M solution of NaOH, Na_2CO_3 , NaHCO_3 , or HCl for the test. The conical flask containing the reaction mixture was shaken at 150 rpm for 24 h at room temperature. The suspensions were subsequently filtered using a $0.45 \mu\text{m}$ filter. The filtrate (10 ml) was back-titrated against a 0.01 M HCl standard solution to determine the hydroxyl group content. The content of the basic groups was determined by back-titration of the filtrate with 0.01 M NaOH. This was performed by agitating 0.1 g of biomass in a 0.01 M HCl solution for 24 h.

pHPZC: Adding 0.1 g of BRSP to a 0.01 M NaCl solution enabled the measurement of the pH point of zero charge (pHpzc) of the BRSP. NaCl solutions with different pH levels were prepared. The pH levels were adjusted to 1 to 12 (± 0.1 pH unit) using 0.1 M HNO₃ and 0.1 M NaOH solutions. The mixtures were placed on a rotary shaker at 150 rpm and shaken for 72 h. The pH_f (pH after settling) was then measured. The PZC was determined by plotting the differences in pH ($\Delta\text{pH} = \text{pH}_f - \text{pH}_i$) versus the initial pH (pH_i) [46].

2.1.4 Structural and physicochemical characterization of *B. Racemosa* sawdust

The surface morphology, elemental composition, chemical structure, and textural properties of the synthesized adsorbents were fully characterized using SEM-EDX, FT-IR, and BET analyses. The surface morphology of the adsorbents was studied using Scanning Electron Microscopy (SEM) (Quanta 200-EDX, India), conducted as per standard procedures, at an accelerating voltage of 5.00 kV. The elemental composition and atomic distribution were measured using EDX (Quanta 200 F-EDS system). Fourier-transform infrared (FT-IR) spectroscopy (Shimadzu IR-Spirit) was employed to determine the functional groups of the biosorbents before and after Cr(VI) adsorption, in the scanning range of 4000–400 cm⁻¹. Key vibrational modes related to the functional group interactions were noted. The surface area was evaluated using the Brunauer–Emmett–Teller (BET) method (BELSORP Mini X, India). Nitrogen gas adsorption–desorption at 700 mmHg (atmospheric pressure) was performed after degassing the sample at 350 °C for five hours. The BET surface area and pore size were measured to determine the porous structure of the biosorbents.

2.1.5 Adsorption isotherms, kinetics, and thermodynamic analysis

Adsorption isotherms, kinetics, and thermodynamics provide in-depth insights into the adsorption process, which aid in developing effective techniques for removing heavy metals [47]. The adsorption isotherms of several models, including the Langmuir, Freundlich, Temkin, and Dubin-Radushkevich (D-R), were examined. Based on these isotherms, the applicable factors of the adsorbent surface properties, adsorption mechanism, and adsorbate-adsorbent interactions were defined [48]. The Freundlich model is appropriate for multilayer adsorption on heterogeneous surfaces with varying adsorption energies [48, 49]. In contrast, the Langmuir isotherm is employed for monolayer adsorption on a uniform surface [50]. The Temkin isotherm illustrates the impact of indirect interactions between the adsorbate and adsorbent [51, 52]. Whereas the D-R model offers insights into the energy of adsorption, whether it involves physical or chemical adsorption [53, 54].

The adsorption kinetics study examines the adsorption of heavy metals onto adsorbents. According to Lagergren's formula, the pseudo-first-order model states that the adsorption rate depends on the difference between the equilibrium adsorption capacity [52, 55]. The pseudo-second-order model suggests a chemisorption process, with the overall rate proportional to the number of available adsorption sites [56, 57]. Efficient adsorption systems are designed based on kinetic models, which provide information on adsorption rates, equilibrium capacities, and adsorption patterns. In addition, the adsorption process is primarily governed by thermodynamics, due to its feasibility and spontaneity. By analyzing thermodynamic parameters such as Gibbs free energy (ΔG),

enthalpy (ΔH), and entropy (ΔS), the endothermic or exothermic nature of adsorption can be determined, and the predominant parameter in the adsorption process can be identified [55, 58, 59].

3 Results and discussion

3.1 Adsorption behaviour and batch study findings

3.1.1 Influence of biosorbent size

In order to explain the effect of particle size of adsorbent on the removal of Cr(VI), biomass fractions between 75 and 425 μm were screened systematically. A sharp negative correlation was found between particle size and removal efficiency. As particle size decreased, the adsorption of Cr(VI) increased significantly from 40% to approximately 99%. This is due to the enhanced surface area and higher accessibility of adsorption sites in smaller particles, resulting in more efficient and quicker adsorption of metal ions. The smallest particle size (75 μm) resulted in practically complete removal of Cr(VI), emphasizing its better adsorption capability. The largest particle size (425 μm) showed drastically compromised performance, with efficiency in removal falling to ~41%. These results underscore the pivotal role of particle size optimization in achieving optimal efficacy of biosorbents for heavy metal remediation. The trend, as demonstrated in Fig. 2, substantiates that adsorption efficiency is at its highest at the smallest particle size considered, confirming the vital role of surface area and diffusion dynamics in biosorption processes. For further studies, the 75 μm biomass fraction, which exhibited the greatest Cr(VI) removal capacity, was used as the reference particle size for the adsorbent.

3.1.2 Influence of pH

Figure 3 depicts how solution pH (1–12) affects BRSP's tendency to biosorb Cr(VI) from aqueous medium. A prominent pH dependence was observed: Cr(VI) removal rate was consistently higher (~90–99%) under acidic conditions (pH 1–5); however, efficiency declined sharply above pH 6, with minimal uptake at alkaline pH (>9). These findings indicate that solution pH plays a pivotal role in controlling Cr(VI) uptake due to its dual

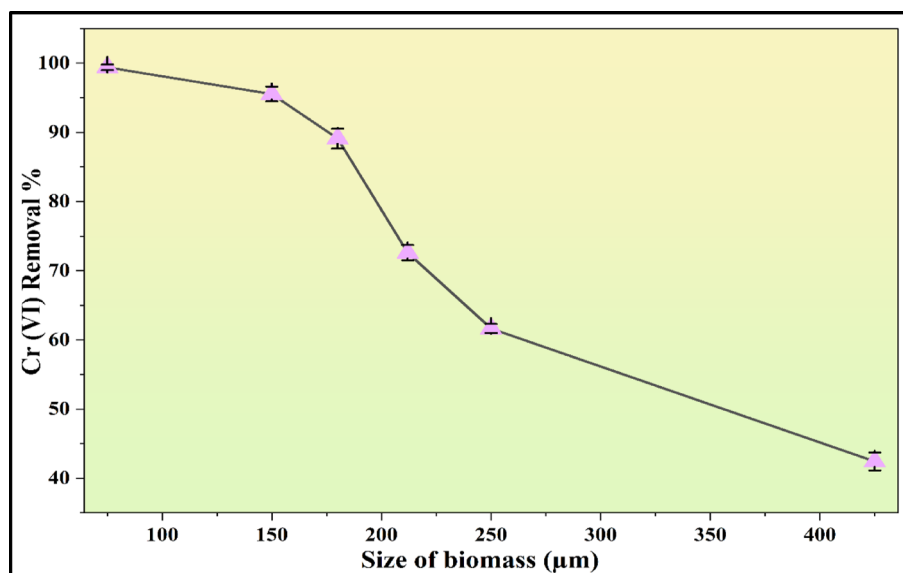


Fig. 2 Effect of BRSP particle size on Cr(VI) removal efficiency

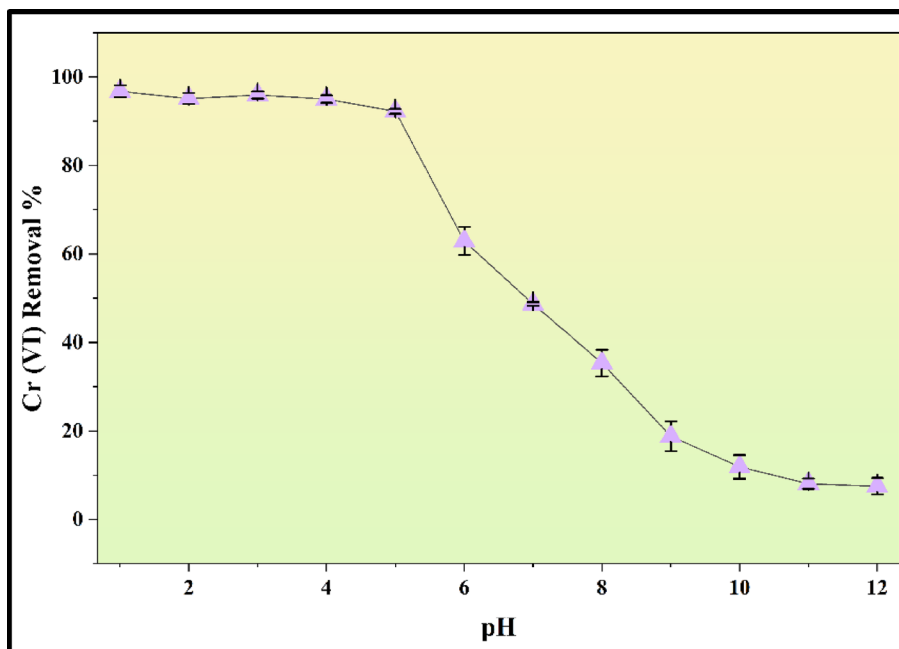
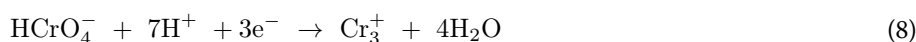


Fig. 3 Effect of pH on Cr(VI) removal efficiency by BRSP

influence on (i) the surface charge characteristics of BRSP and (ii) the aqueous medium speciation behaviour of chromium. At low pH, the BRSP surface becomes protonated, acquiring a net positive charge, which strongly favours the electrostatic attraction of negatively charged Cr(VI) oxyanions such as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. Protonation also enhances ion-exchange interactions between surface functional groups ($-\text{OH}$, $-\text{COOH}$) and Cr(VI) species. The dominance of HCrO_4^- in acidic solutions further promotes adsorption through electrostatic interaction and possible reduction pathways. The reduction of Cr(VI) to Cr(III) at the adsorbent interface is also facilitated under strongly acidic conditions, as shown in Eqs. (7–8):



At moderate pH, the following reaction occurs:



In contrast, when the pH exceeded 6, the surface of BRSP became progressively deprotonated, resulting in electrostatic repulsion between negatively charged sites and $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ species. Simultaneously, hydroxide ions increasingly competed with Cr(VI) oxyanions for binding sites, thereby reducing the effective adsorption. At $\text{pH} > 9$, removal efficiency dropped to nearly zero, which may also be partly attributed to the tendency of Cr(VI) species to remain stable in solution and the reduced availability of protonated functional groups on BRSP.

Overall, these findings demonstrate that acidic conditions strongly promote Cr(VI) removal, with pH 4 identified as the optimum for subsequent experiments. The observed trends are consistent with previous reports on lignocellulosic biosorbents [60, 61], where electrostatic attraction, competitive adsorption with protons, and Cr(VI) speciation collectively governed the removal process.

At lower pH levels, the high concentration of H^+ ions on the surface of the adsorbent enhanced the reduction of dichromate ions ($Cr_2O_7^{2-}$). However, when the pH exceeded 6.0, the adsorption decreased significantly. This reduction is due to the interference between chromate ions (CrO_4^{2-}) and hydroxide ions (OH^-), as the adsorption of OH^- ions takes precedence. Biosorption is favorable at lower pH levels. BRSP demonstrated the most effective Cr(VI) removal at a pH of 4.0. Therefore, pH 4 (optimal pH) was identified for further research. The efficiency declined as pH values increased. This can be explained by the combined effect of adsorbent surface charge and Cr(VI) species formation. Both these factors work together to influence the adsorption process. At low pH, the BRSP surface gets protonated, which increases the electrostatic attraction with $HCrO_4^-$ ions. This enhanced attraction occurs because $HCrO_4^-$ is the main chromium species present under acidic conditions. In alkaline conditions, we observe that the surface charge becomes less positive, and the main chromium species only face repulsive forces, which reduces their adsorption on the surface. The observed trend shows that electrostatic interactions and proton competition control Cr(VI) uptake. This finding matches previous studies on lignocellulosic adsorbents.

3.1.3 Influence of the quantity of biomass

The biomass quantity (BRSP) significantly impacts and plays a critical role in Cr(VI) elimination efficacy, as illustrated in Fig. 4. Primarily, it is due to the availability of adsorption sites and the sufficient surface area. An increase in dosage of biomass from 0.25 g to 2.0 g caused a marked improvement in removal efficiency, reaching a peak of 99% at approximately 1.0 g. This enhancement is attributed to the larger number of adsorption positions. However, beyond this optimal dosage, further increase led to a decline in adsorption capacity ($mg\ g^{-1}$), likely due to particle overlapping and aggregation, which decreases the accessible surface area and leaves some reactive sites inactive

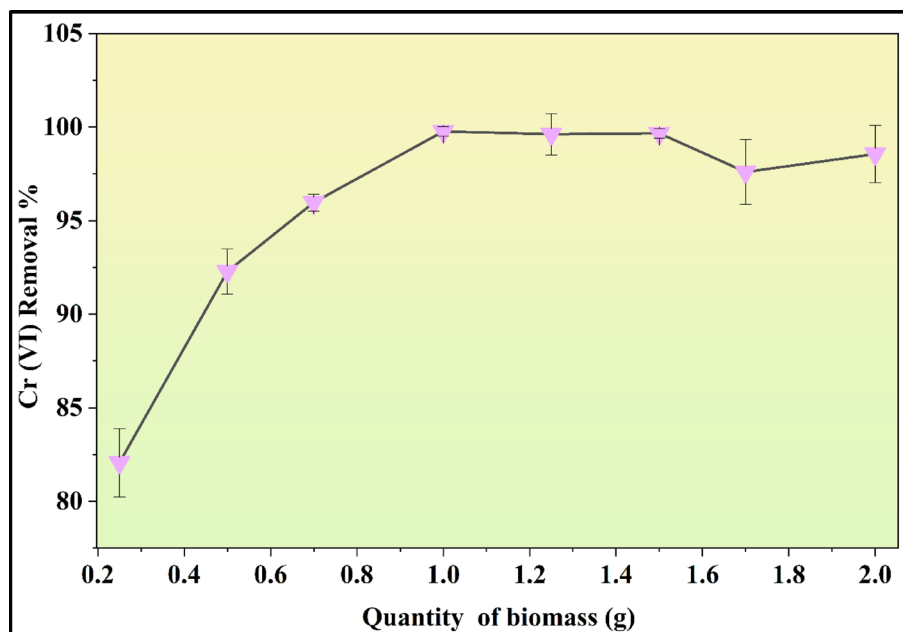


Fig. 4 Effect of quantity of BRSP on Cr(VI) removal efficiency

[62, 63]. This saturation effect specifies that excessive adsorbent does not proportionally improve removal, as Cr(VI) ions in solution become.

limited. Biomass quantity ranging from 0.5 to 2.0 g demonstrates consistently high removal percentages, aligning with earlier research. For subsequent experiments, an optimal dose of 0.5 g was selected, balancing high removal efficiency with resource economy and sustainability. These results emphasize the relevance of dosage optimization in large-scale applications to expand performance while minimizing resource utilization.

3.1.4 Influence of concentration

The initial Cr(VI) concentration played a significant role in determining both the capacity and efficiency of the biosorption process, as shown in Fig. 5. Experiments were carried out over the concentration range 5–300 mg/L using a fixed biomass dose of 0.5 g with controlled conditions (pH 4.0, solution volume of 100 mL, ambient temperature). At lower concentrations of 5 and 10 mg/L, BRSP showed outstanding removal capacities of 99.87% and 99.75%, respectively, reflecting the presence of high availability of active binding sites for Cr(VI) ions.

With an increase in initial concentration, a significant reduction in percentage removal was noticed. This is because of the continuous saturation of adsorption sites, which restricts subsequent metal adsorption despite the higher driving force for mass transfer. Although there was an improvement in adsorption capacity (mg g^{-1}) at elevated concentrations because of higher collision frequency and mass transfer kinetics, overall removal efficiency decreased, which indicates that equilibrium between adsorbent and adsorbate had been reached.

These results agree with the Langmuir isotherm model, which gave the optimum fit to the experimental data, verifying monolayer adsorption onto a homogeneous surface.

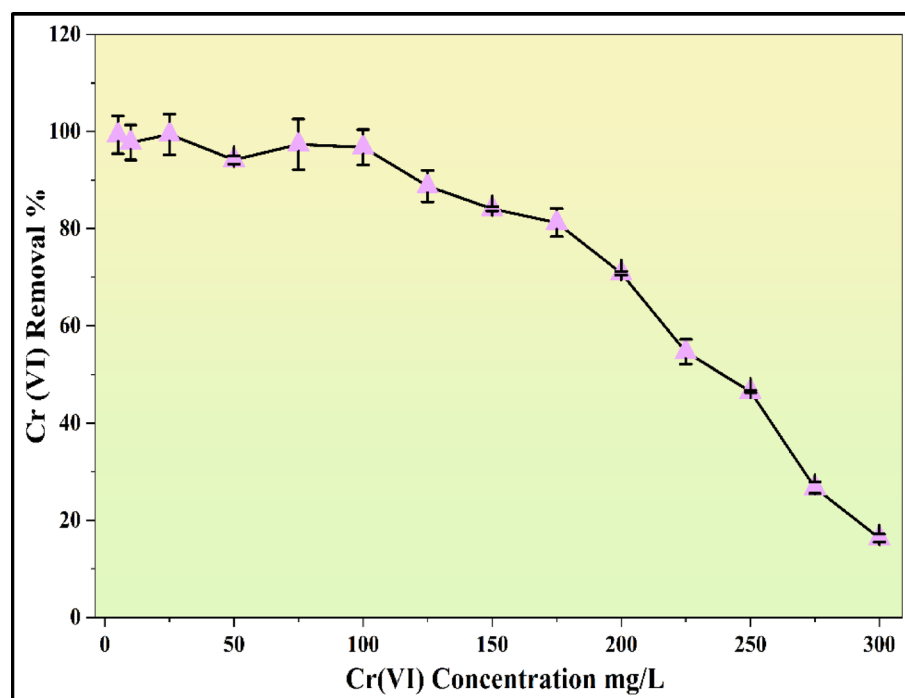


Fig. 5 Effect of Cr(VI) concentration on Cr(VI) removal efficiency by BRSP

The saturation phenomenon at high Cr(VI) levels underscores the need for optimising initial metal ion concentrations to achieve optimal biosorption performance.

3.1.5 Influence of contact time

Contact time is a crucial parameter that significantly influences the efficiency of adsorption. In this research, the biosorption kinetics of Cr(VI) onto BRSP were studied within a time interval of 10 to 210 min to establish the most favorable time for equilibrium. As in Fig. 6, the removal of Cr(VI) accelerated in the initial time interval, and 24.92% was removed within the first 10 min. The rate of adsorption increased further, reaching a plateau of ~60 min with a maximum removal efficiency of around 99%.

This rapid adoption is attributed to the large number of accessible binding sites on the biomass surface, which enables rapid contact between Cr(VI) ions and hydroxyl, carboxyl, and amine groups. After 60 min, the rate of removal leveled off, which means saturation of accessible sites and attainment of adsorption equilibrium. The trend observed exhibits a common two-stage kinetic process: rapid adsorption followed by slow convergence towards equilibrium.

Kinetic modeling indicated that the data were best represented by the pseudo-second-order equation, implying that chemisorption, involving electron sharing or exchange, is the prevailing mechanism controlling Cr(VI) adsorption. The site-specific preference of Cr(VI) ions for functional groups also supports this inference, underscoring the importance of chemical interactions in biosorption. These results underscore the importance of maximizing removal efficiency by optimizing contact time and minimizing operating costs. For all other experiments, a contact time of 60 min was chosen as the optimal time for Cr(VI) biosorption.

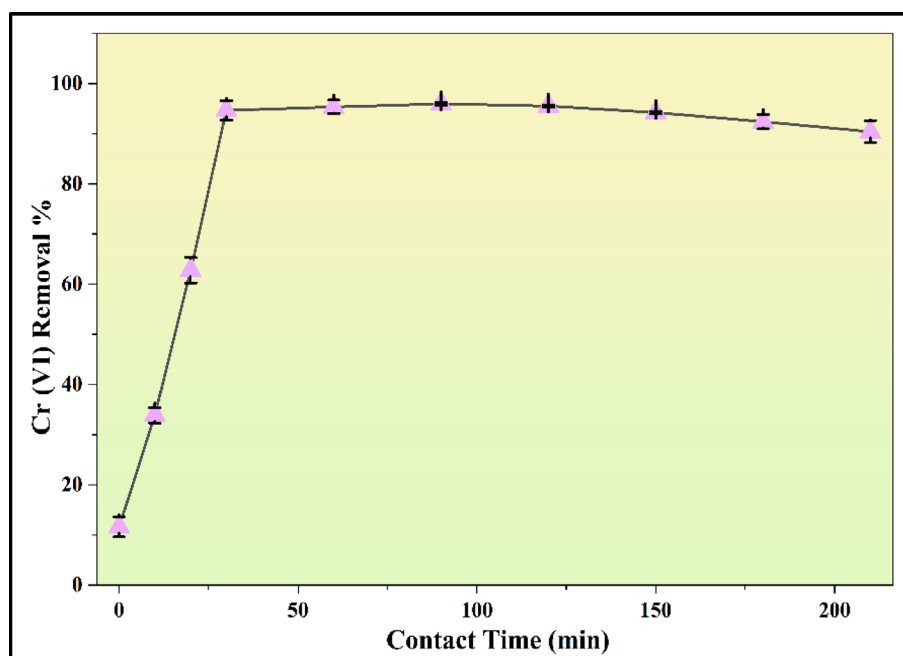


Fig. 6 Effect of contact time on Cr(VI) removal by BRSP

3.1.6 Influence of volume of solution

As shown in Fig. 7, the removal of Cr(VI) was extremely efficient, over 95% when the solution volume was maintained at 125 mL. When the volume was increased above 150 mL, there was a dramatic decrease in removal efficiency, reaching approximately 43% at 250 mL.

This decrease is mainly contributed by the saturation of the adsorption sites on the biosorbent surface due to the higher concentration of Cr(VI) ions, which overcomes the binding capacity of the biomass. Moreover, larger solution volumes tend to decrease the contact time between the metal ions and the adsorbent, thereby reducing the potential for equilibrium adsorption to occur. The decreased concentration gradient at increased volumes also reduces the driving force for mass transfer, thus decreasing the total adsorption rate.

These results highlight the importance of achieving an optimal solution volume to maximize biosorbent capacity. Practically, it emphasizes the requirement for scaling the adsorbent dose and adjusting operation parameters proportionally to solution volume to avoid loss of efficiency. On the basis of the experimentally obtained data, the optimum volume range for maximum removal of Cr(VI) under the given conditions is 25–125 mL. For uniformity in future experiments, a volume of 100 mL was chosen for the solution.

3.1.7 Influence of temperature

The impact of temperature on Cr(VI) biosorption was examined over the range of 293–333 K to evaluate its influence on removal efficiency and to supplement the thermodynamic evaluation. As indicated by Fig. 8, the removal efficiency for Cr(VI) increased consistently with temperature, from 91.22% at 293 K to 97.91% at 333 K. This improvement reveals that higher thermal energy promotes greater interactions between Cr(VI) ions and BRSP active sites, thereby enhancing both the adsorption capacity and kinetics.

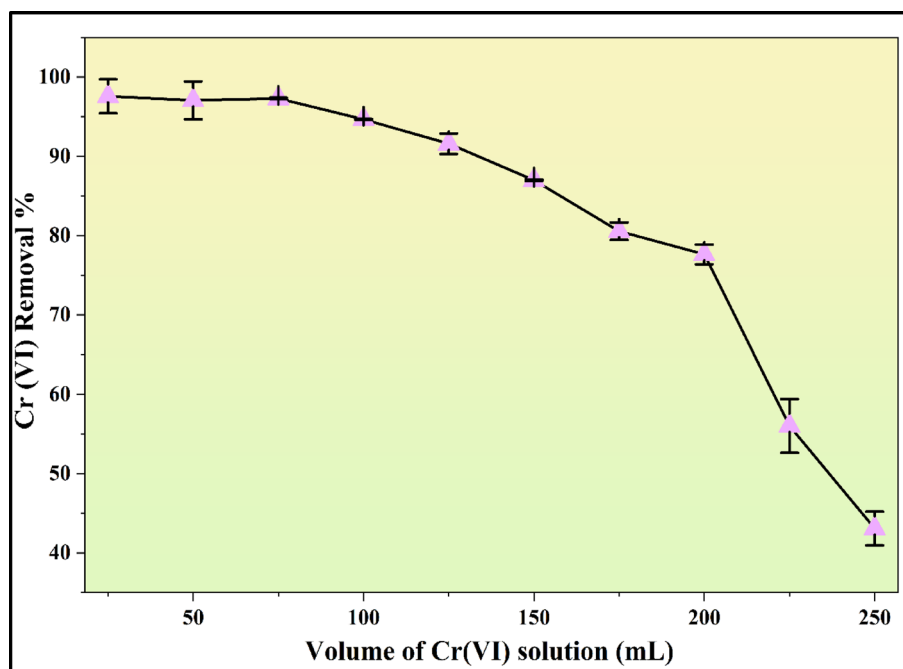


Fig. 7 Effect of Cr(VI) solution on Cr(VI) removal by BRSP

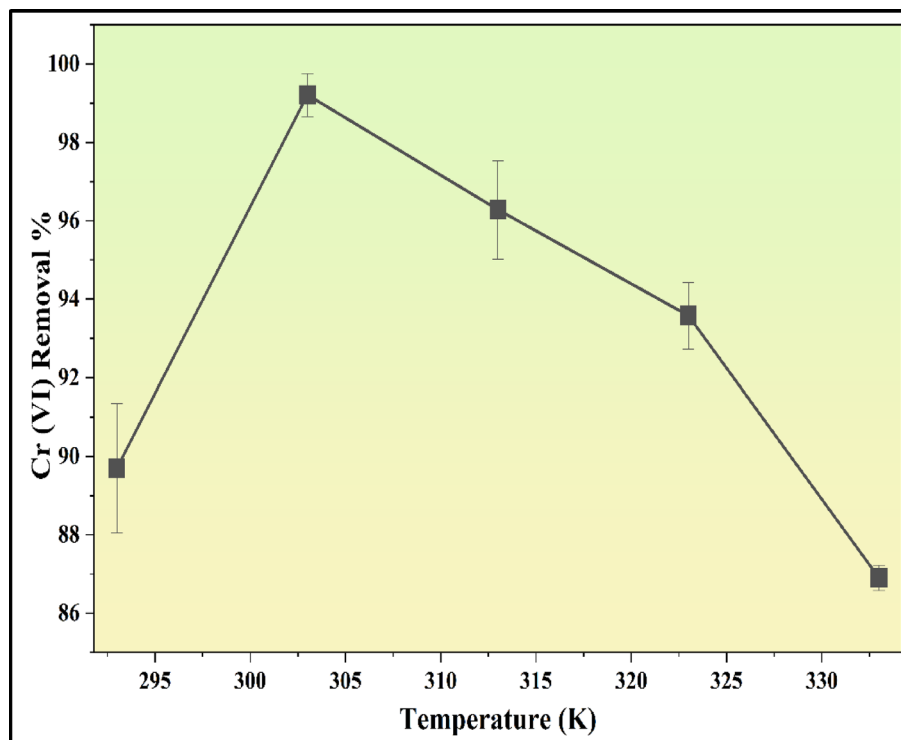


Fig. 8 Effect of temperature on Cr(VI) removal by BRSP

Table 2 Physicochemical properties of BRSP

Parameters	Values
Moisture (%)	4.56
Ash (%)	7.04
Volatile matter (%)	60.31
Fixed carbon (%)	28.09

The trend from observation agrees with the thermodynamic parameters calculated from the van't Hoff analysis. The negative Gibbs free energy values (ΔG^0) at all temperatures validate the spontaneity of the adsorption process. The positive enthalpy change ($\Delta H^0 = 34.42 \text{ kJ}\cdot\text{mol}^{-1}$) suggests that the biosorption is endothermic, and increased uptake is favored by higher temperatures. Moreover, the positive entropy change ($\Delta S^0 = 1.77 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) also indicates greater randomness at the solid-liquid interface, which is probably because of the replacement of water molecules and greater mobility of Cr(VI) ions in the process of adsorption.

Together, the thermodynamic and experimental findings confirm that temperature is a critical determinant in increasing Cr(VI) biosorption by BRSP. The process is not only favored thermodynamically but also kinetically enhanced at higher temperatures, rendering BRSP a viable candidate for field applications in fluctuating thermal conditions.

3.2 Analysis of the elemental composition of the adsorbent

3.2.1 Proximate analysis

The results of the proximate analysis of the biomass are presented in Table 2. The results indicate a low moisture level in the sample, which is advantageous as it enhances the availability of active sites for adsorption without requiring considerable drying.

Moderate ash concentrations indicate the presence of inorganic elements that may require management and positively affect the adsorption [64]. The significant amount of volatile matter suggests creating a porous structure by subjecting the material to heat or chemical treatment. This increases the available surface area for the adsorption [65]. A substantial amount of fixed carbon ensures a robust framework with numerous active sites, which is essential for the efficient adsorption of heavy metal ions. This investigation demonstrates that subjecting biomass to suitable pre-treatment and activation can be an efficient and environmentally friendly method for removing heavy metals from wastewater.

3.2.2 Surface chemistry sorbent

The examination of the surface chemistry of BRSP indicated the presence of functional groups crucial for its action as a biosorbent. The carboxyl groups were measured to be 0.164 meq/g, indicating their acidic properties, capacity to bond with metal ions, and proton donation ability. Phenolic groups provide an extra level of acidity at a rate of 0.056 meq/g, which increases the possibility of hydrogen bonding interactions with pollutants. The most prevalent groups in the biomass, with a concentration of 0.680 meq/g, were lactonic groups, namely, lactones and lactols. These groups enhance the reactivity of biomass owing to their cyclic nature [66]. The sawdust surface exhibited a collective concentration of acidic groups of 0.900 meq/g and a concentration of fundamental groups of 0.465 meq/g, respectively.

This suggests the presence of fundamental functional groups that may interact with anions or act as exchange sites. The chemical composition of sawdust powder renders it suitable for applications that require contaminant elimination. Their acidic functional groups facilitate effective adsorption, particularly for eliminating heavy metals from aqueous environments. The specific concentrations of the functional groups are presented in Table 3.

3.2.3 Point zero charge (pHPZC)

Figure 9 shows the relationship between pH and pHPzc values. From the graph, it is clear that the pHPzc values are lower than the pH values. The adsorbent developed positive charges, which enhanced its effectiveness in eliminating Cr(VI) anions. Likewise, when the pH exceeds the pHPzc ($7 > 2.7$), as shown in Table 3, the adsorbent acquires positive charges that greatly enhance the removal of Cr ions. This phenomenon can be explained by the intense electrostatic attraction between the positively charged surface of the adsorbent and dichromate ions.

In an acidic environment, the predominance of the chromate anion (HCrO_4^-) over the dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$) enhances the adsorption efficiency of these species [67]. These findings are consistent with those reported by Mancilla et al., [68]. Owing to the

Table 3 Surface chemistry of BRSP

Functional groups	Values (meq /g)
Carboxyl	0.164
Phenolic	0.056
Lactonic (lactones & lactols)	0.680
Total acidic	0.900
Total basic	0.465
pH PZC	2.7

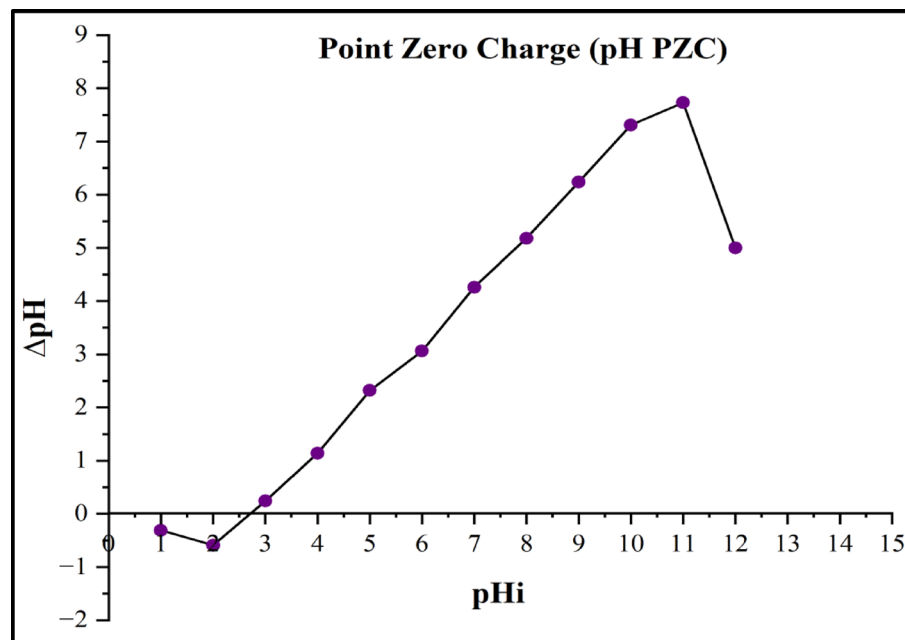


Fig. 9 Determination of pH_{pzc} of BRSP

Table 4 BET analysis of BRSP

Sample pore	SBET (m ² /g)	Pore volume(cm ³ /g)	Average pore diameter (nm)
BRSP	212.2	0.323	6.403

strong electrostatic interactions, the BRSP surface chemistry, characterized by substantial acidic functional groups and pH PZC, enhances its effectiveness as a biosorbent for Cr(VI) ions.

3.3 Characterization analysis

3.3.1 BET (Brunauer–Emmett–Teller)

The texture of (BRSP) was studied by BET (Brunauer–Emmett–Teller (BET) surface area analysis, and the results are shown in Table 4. The specific surface area (SBET) of BRSP was 212.2 m²/g, suggesting that a large surface area was available for adsorption. Indicating more active surface sites for binding. The total pore volume of BRSP was 0.323 cm³/g, indicating the presence of considerable internal pores through which adsorbate molecules can diffuse into the sorbent matrix. The average pore diameter was estimated to be 6.403 nm from the graph, indicating the mesoporous characteristics of BRSP, as the value falls within the range of mesopores (2–50 nm). Mesoporous structures have special advantages in adsorbing heavy metal ions from aqueous solutions because their surface accessibility and internal surface area can be optimized. Overall, BET analysis indicated that BRSP has a high surface area and mesoporous structure, which can effectively contribute to a high biosorption efficiency for heavy metals, including Cr(III) and Cr(VI), from electroplating wastewater.

3.3.2 Surface morphology

As shown in Fig. 10A (500X, 200 μm), raw BRSP displays elongated fibrous structures, characteristic of wood cellulose, which are loosely arranged with a naturally porous and

slightly rough texture. The lower magnification image (100X, 100 μm) also verifies its natural sponge-like structure (which is favorable for adsorption).

After loading Cr(VI) for adsorption (Fig. 10B), morphological changes were observed. At 500X, a clear striated pattern of the fiber surfaces was observed, indicating the accumulation and interaction of Cr(VI) with the adsorbent matrix. In addition to the larger surface roughness, visible depositions were observed in the 100X image. The pore volume also decreased, which can be attributed to the partial or total blockage of pores by the Cr(VI) particles. Decreased pore volume may enhance the surface activity and increase the proportion of accessible adsorption sites in the adsorbent.

3.3.3 EDX (Energy-dispersive X-ray spectroscopy)

The elemental composition of BRSP was examined using energy-dispersive X-ray spectroscopy (EDX). The EDX analysis results of the BRSP biomass before and after the addition of Cr(VI) are shown in Fig. 5 (A) and (B).

The EDX spectra of chromium-loaded BRSP demonstrated the presence of a chromium peak, confirming the potential of BRSP as a biosorbent. The tables in Fig. 11 (A) and (B) are shown in the quantitative results of the EDX analysis of the BRSP biomass before and after Cr(VI) adsorption. The EDX analysis indicated that chromium was present at a quantity of 0.6%. The EDX images and tabular data demonstrated the adherence of Cr(VI) to the biomass surface. O, Si, and Al are the most common elements. EDX revealed the presence of Si, which may be attributed to impurities such as dust particles, and Al, which was present at low levels owing to sample coating at the time of analysis [69].

3.3.4 FTIR (Fourier-transform infrared spectroscopy)

IR spectroscopy is an effective analytical method for identifying the chemical components of biomaterial surfaces. This technique provides essential insights into the bonding relationships between the sorbate (metal) and the sorbent (biomaterial). FTIR spectral analysis of BRSP was performed before and after Cr(VI) adsorption from an aqueous medium. Figure 12 shows the comparative peaks obtained for the raw BRSP and chromium-laden BRSP.

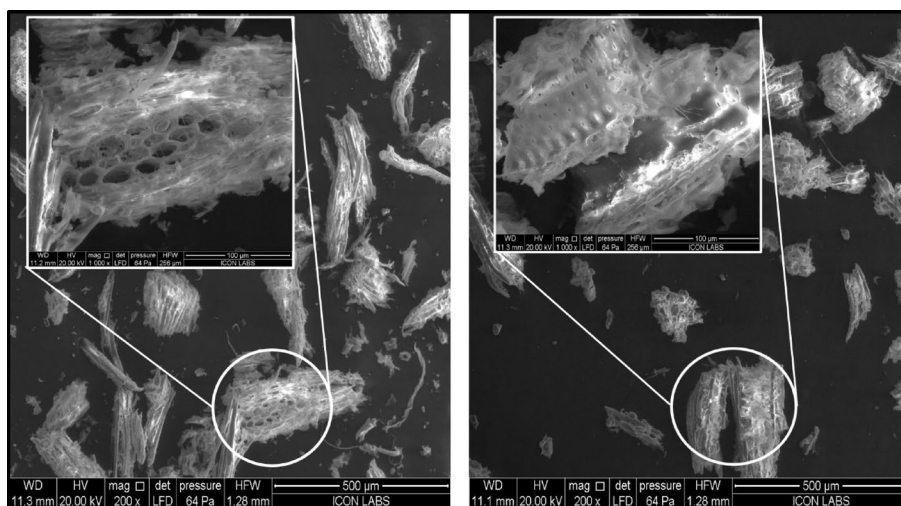


Fig. 10 SEM images of BRSP (A) before and (B) after Cr(VI) adsorption

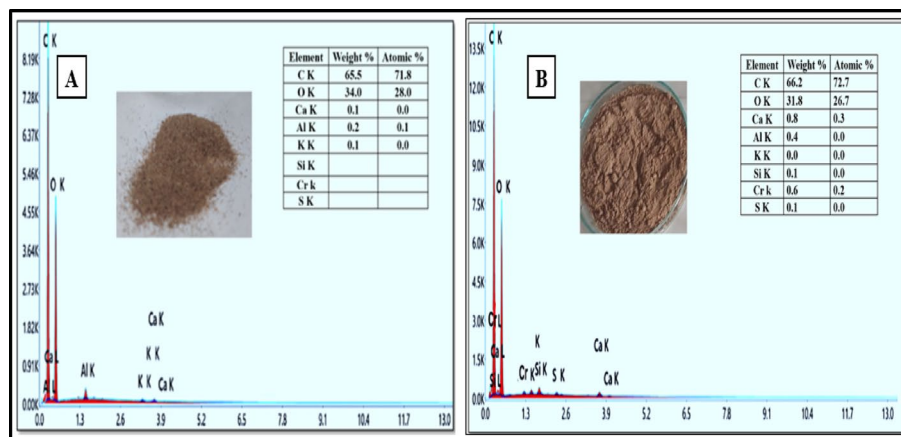


Fig. 11 EDX images (A) before and (B) after Cr(VI) on BRSP

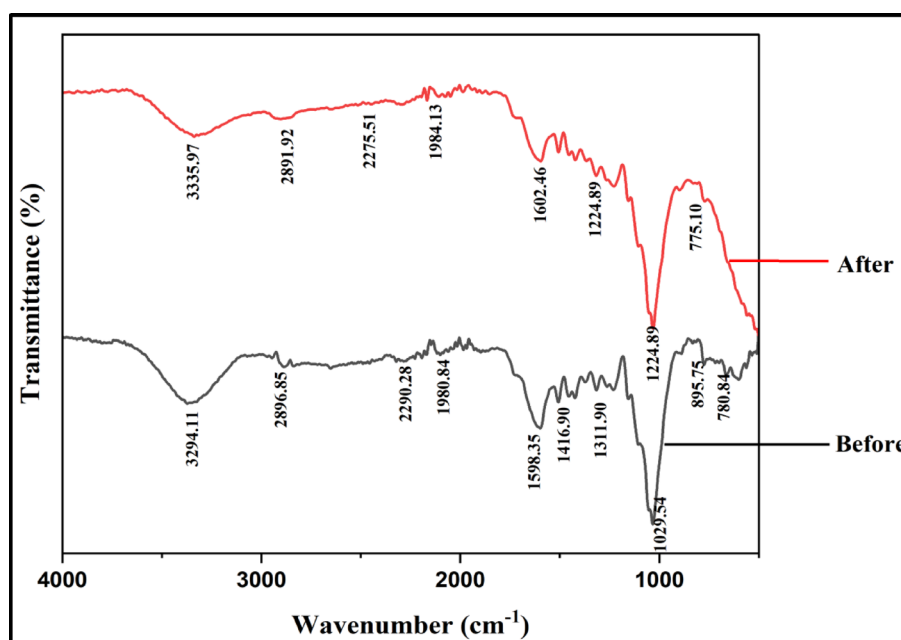


Fig. 12 FTIR image of biomass before and after Cr(VI)

The FT-IR spectrum of *Bauhinia racemosa* sawdust powder (BRSP) exhibited several absorption bands, indicative of the chemical complexity of the biomass. The broad hydroxyl (-OH) peak shifted from 3335.97 cm^{-1} before adsorption to 3294.11 cm^{-1} after adsorption, indicating a change in hydrogen bonding due to the interaction with Cr(VI) [70]. The contribution from the aliphatic C–H stretching observed at 2891.92 and 2896.85 cm^{-1} suggests the existence of cellulose and hemicellulose, and their slight shifting is evidence of interaction between Cr(VI) and the carboxyl group [71]. Peaks at approximately 2275.51 and 2290.28 cm^{-1} were presumably assigned to the formation of a complex between chromium ions and the $\text{-N}=\text{C}=\text{O}$ groups [72]. Carboxyl-associated C=O vibrations (from 1602.46 to 1598.35 cm^{-1}) indicate Cr binding to functional groups such as -COOH [73, 74]. To further understand the influence of these functional groups on adsorption efficiency, the FTIR results were analyzed in terms of their specific roles in Cr(VI) binding. Basically, FTIR analysis showed that BRSP has the same

main functional groups as $-\text{OH}$, $-\text{COOH}$, $-\text{NH}$, $\text{C}=\text{O}$, and aromatic groups from cellulose, hemicellulose, and lignin that are responsible for Cr(VI) adsorption. As per the results, the wide $-\text{OH}$ stretching band shifted after adsorption, showing its main role in hydrogen bonding with Cr(VI) . This indicates that $-\text{OH}$ groups help in surface binding regarding the removal process. Carboxyl groups show shifts in $\text{C}=\text{O}$ and COO^- bands, which further provide strong binding sites for metal ions. The adsorption efficiency improves through ion exchange and chelation mechanisms. The changes in the amine and $\text{N}=\text{C}=\text{O}$ bands indicate that nitrogen groups play a crucial role in forming metal-ligand complexes. These nitrogen groups definitely improve selective binding with chromium species. The changes in aromatic $\text{C}-\text{H}$ bands show π -electron interactions. These interactions help stabilize the adsorption of Cr(VI) onto BRSP. The hydroxyl, carboxyl, carbonyl, and aromatic groups in BRSP work together to bind Cr(VI) very well. These groups definitely increase the number of active sites and help in binding and reducing the metal effectively. We are seeing that FTIR results show the chemical makeup of BRSP, with many oxygen and nitrogen groups, directly controls how well it can remove Cr(VI) from water. This shows that BRSP works as a good biosorbent because of these special chemical groups.

The 1507.25 and 1503.14 cm^{-1} peaks indicate the intermolecular interactions between the carboxyl, hydroxyl, and amine groups for Cr(VI) adsorption [61]. In comparison, shifts from 1425.99 to 1416.96 cm^{-1} and 1330 to 1371 cm^{-1} reveal the role of carbohydrate and $\text{C}-\text{H}$ rocking vibrations, respectively [75]. The $\text{C}-\text{O}$ bands observed at 1224.89 and 1225.71 cm^{-1} showed a slight shift, and the $\text{C}-\text{O}$ peak shifted from 1033.65 to 1029.54 cm^{-1} , indicating that Cr(VI) is bound to hydroxyl and carboxyl groups [76]. Displacement of the dichromate-related $\text{Cr}-\text{O}$ peak from 900 cm^{-1} to 899 cm^{-1} confirmed the binding of Cr(VI) onto BRSP [77]. Aromatic $\text{C}-\text{H}$ at 775.10 cm^{-1} were also shifted to 780.84 cm^{-1} for aromatic bonds, which proved interaction of chromium with aromatic groups. These spectral shifts agreed with the Boehm titration findings, which verified the direct involvement of cellulose and hemicellulose functional groups in Cr(VI) adsorption and suggested significant surface chemistry changes in BRSP after Cr(VI) adsorption [78].

3.4 Isotherm model

The adsorption isotherms indicate an equilibrium relationship between Cr(VI) ions and BRSP. The adsorption behaviour was analysed using four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R)), and their parameters are listed in Table 4, and plots are shown in Figs. 13, 14, 15 and 16.

3.4.1 Langmuir adsorption isotherm model (2-parameter model)

Numerous authors have utilized the Langmuir isotherm model to explain adsorption phenomena. Its purpose is to depict monolayer adsorption on a uniform surface with a limited number of identical sites. The adsorbed molecules did not interact, and the adsorption of one molecule did not affect the adsorption of the other. The adsorption process is reversible, with an equilibrium between the adsorbed and free molecules in the solution.

Mathematical expression for Langmuir (linear form).

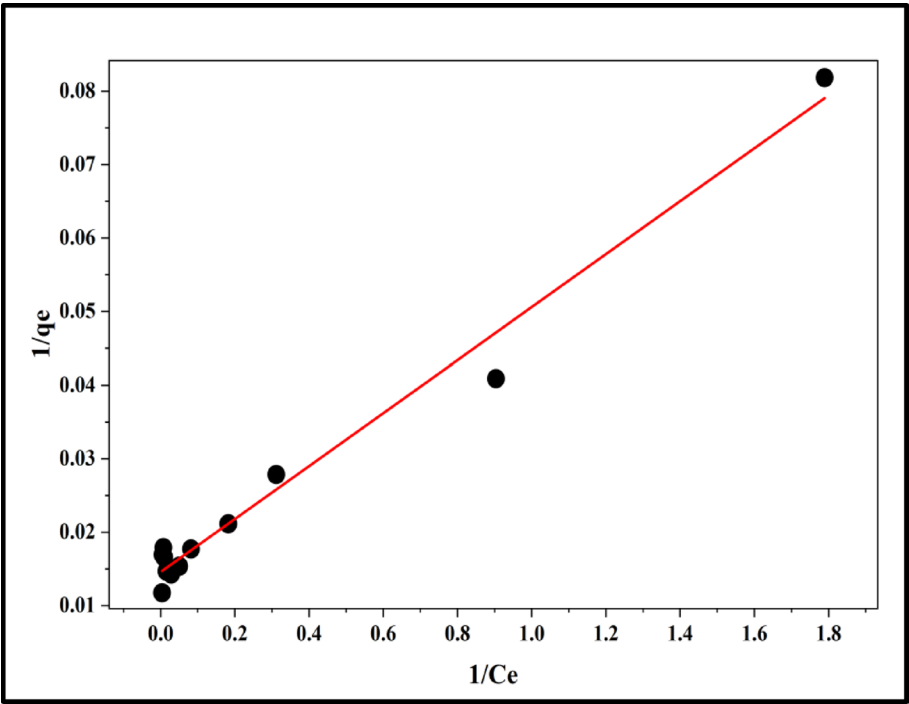


Fig. 13 Langmuir adsorption isotherm study for removal of Cr(VI) using BRSP

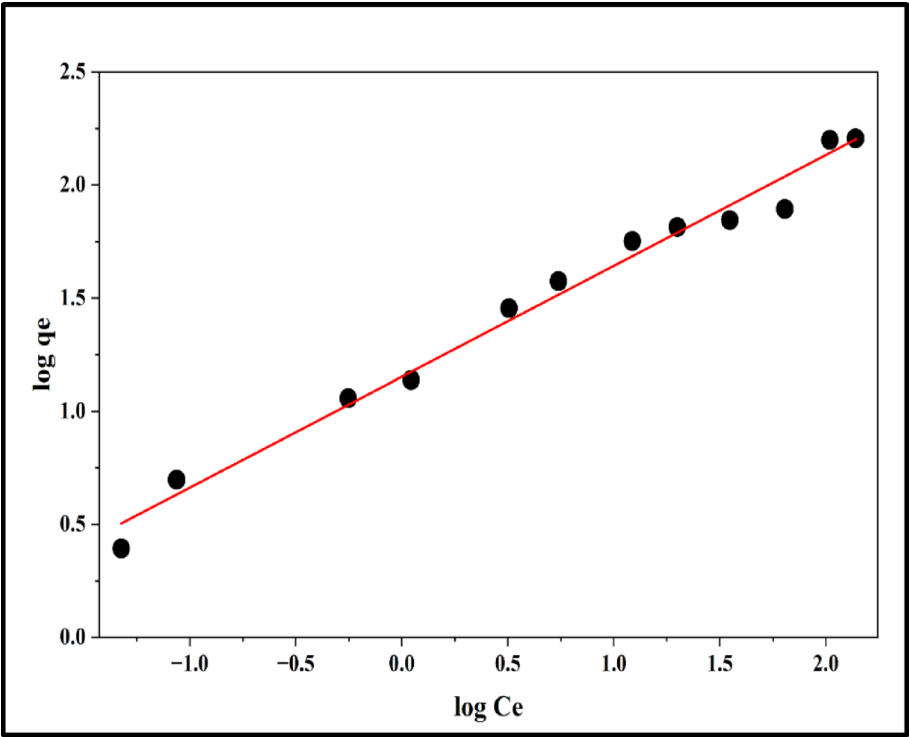


Fig. 14 Freundlich adsorption isotherm for the removal of Cr(VI) using BRSP

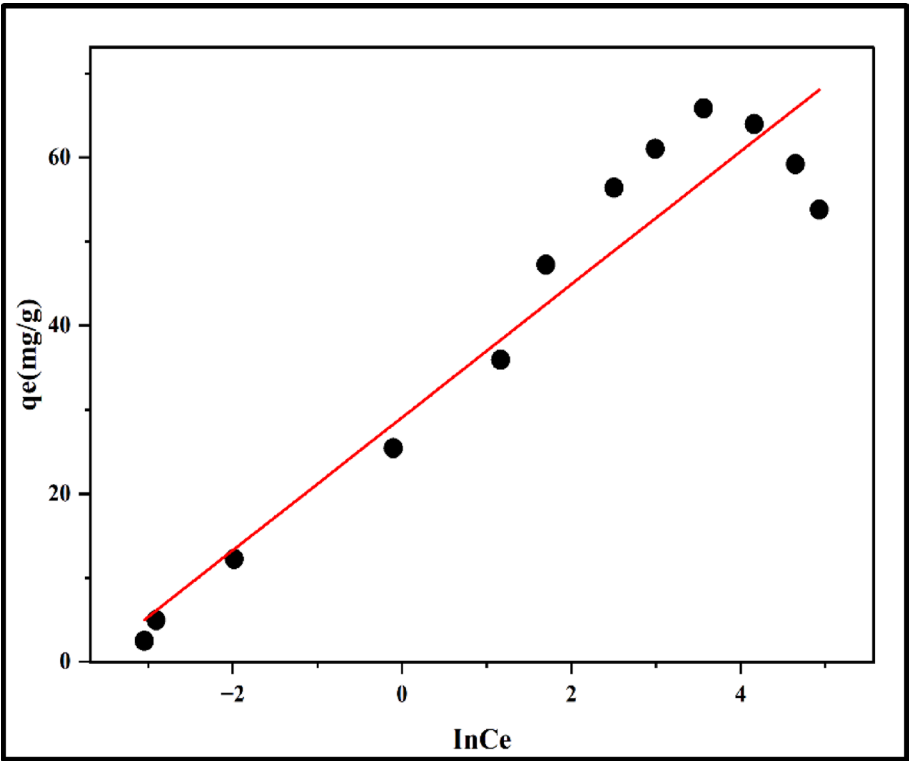


Fig. 15 Temkin adsorption isotherm for the removal of Cr(VI) using BRSP

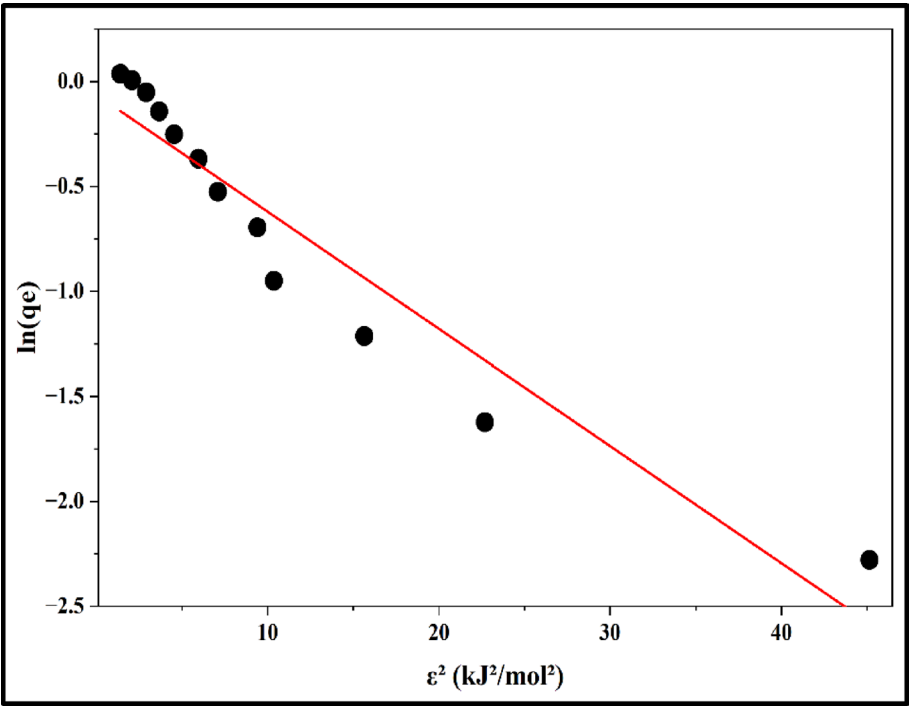


Fig. 16 D-R adsorption isotherm for the removal of Cr(VI) using BRSP

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \quad (9)$$

Where.

q_e = amount of adsorbate adsorbed per unit of adsorbent at equilibrium (mg/g).

q_m = maximum adsorption capacity of adsorbent (mg/g).

C_e = Equilibrium concentration of adsorbate in solution (mg/L).

K_L = Langmuir adsorbate constant (mg/L) related to the affinity between the adsorbate and adsorbent.

The Langmuir model, based on monolayer adsorption on a homogenous surface, best fit the data, with an R^2 (0.99). The theoretical maximum monolayer adsorption capacity (q_{max}) was 106.86 mg/g, which is close to the experimental q_e value (105.61 mg/g), indicating that BRSP can effectively adsorb Cr(VI). The dimensionless separation factor (R_L) was calculated to be 0.0653, indicating the favorability of the adsorption process ($0 < R_L < 1$). As shown in Table 5, the adsorption data fitted best with the Langmuir model because it showed the highest correlation coefficient. This definitely indicates that adsorption happens in a single layer on a uniform surface with similar active sites. This means that the BRSP surface has binding sites with equal energy where each Cr(VI) ion forms stable bonds. Once a site is occupied, no more adsorptions can happen at that particular location. The Langmuir model shows that hydroxyl, carboxyl, amine, and aromatic groups are definitely responsible for specific binding sites, as confirmed by FTIR analysis. The adsorption process occurs in single layers without forming multiple layers or showing significant differences across the surface.

3.4.2 Freundlich adsorption isotherm model (2-parameter model)

Freundlich isotherm is an empirical model that describes the adsorption process on heterogeneous surfaces.

The Freundlich equation is expressed as (linear form).

$$\log q_e = \log k_f + (1/n) \log C_e \quad (10)$$

where,

q_e = The amount of solute adsorbed per unit mass of adsorbent (mg/g).

Table 5 Isotherm and parameters

Isotherm Model	Parameter	Values
Langmuir Adsorption Isotherm (2 Parameters)	q_{max} (mg g ⁻¹)	106.86
	K_L (L mg ⁻¹)	0.286
	R_L	0.0653
	R^2	0.99119
Freundlich Adsorption Isotherm (2 Parameters)	K_f	68.983
	$1/n$	2.07615
	R^2	0.9827
Temkin Adsorption Isotherm (2 Parameters)	B_T (J/mol)	316.98
	K_T (J/mol)	0.315
	R^2	0.92006
Dubinin-Radushkevich (D-R) adsorption isotherm (3 parameters)	β (mol ² /kJ ²)	0.0558
	E (kJ/mol)	2.99
	q_m (mmol/g)	0.9984
	R^2	0.9164

C_e = The equilibrium concentration of solute in solution (mg/L).

K_f = The Freundlich constant indicative of adsorption capacity.

$1/n$ = Freundlich exponent, which indicates the adsorption intensity of the adsorbent.

From Table 5, the value of $1/n$ is greater than that of the Freundlich isotherm, which assumes that the surface of an adsorbent is heterogeneous, with varied affinities and energy levels for.

Two parameters, K_f and n , were used to interpret the Freundlich constant; a higher K_f value indicates a greater adsorption capacity of the adsorbent [79]. The $1/n$ value indicates the favorability of the adsorption process. The adsorption was more linear for $0 < 1/n < 1$, suggesting a uniform surface energy on the adsorbent. A higher $1/n$ value (greater than 1) indicates greater heterogeneity. The heterogeneity of the surface, exponential distribution of the active sites, and energy of the active sites are all defined by the Freundlich isotherm model [80]. From The Freundlich isotherm describes a characteristic in which the adsorption energy decreases logarithmically as adsorption progresses. The Langmuir isotherm, on the other hand, assumes a uniform adsorption energy [81]. Freundlich isotherm allows multilayer adsorption, and adsorbed molecules act as additional adsorption sites. Because the Freundlich isotherm is purely empirical, it lacks a theoretical framework associated with isotherms, such as the Langmuir isotherm [82].

3.4.3 Temkin adsorption isotherm model (2 parameter models)

The Temkin adsorption isotherm model is widely used to describe adsorption processes, particularly on heterogeneous surfaces. This model addresses adsorbate interactions, and by incorporating the heat of adsorption, the adsorption energy can be depicted as decreasing linearly with coverage. When the surface of the adsorbent is not homogeneous, this model can provide more accurate expressions for adsorption phenomena [83].

The Temkin equation is expressed as (linear form).

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (11)$$

where.

C_e = Equilibrium concentration of adsorbate (mg/L).

q_e = Amount adsorbed at equilibrium (mg/g).

A_T = Binding equilibrium constant.

B_T = Binding equilibrium heat constant (J/mol).

T = Absolute temperature (K).

The Temkin model considers adsorbate–adsorbent interactions and assumes that the heat of adsorption decreases linearly with surface coverage. The linear fit ($R^2 = 0.920$) and Temkin binding energy ($B_T = 316.98$ J/mol) support a moderate adsorption strength. This also suggests chemisorption through surface complexation or ion exchange mechanisms.

3.4.4 Dubinin-Radushkevich (D-R) adsorption isotherm model (2-parameter models)

The Cr(VI) using the BRSP Dubinin-Radushkevich (D-R) is often utilized in solid-liquid interfaces to describe adsorption equilibria with two parameters. This is highlighted by its ability to consider the adsorption energy and maximum adsorption capacity [84]. The

D-R isotherm model is an empirical model that describes adsorption on heterogeneous surfaces. This model helps distinguish [85].

The linear form of the D-R isotherm equation is as follows:

$$\ln q_e = \ln q_m - k\varepsilon^2 \quad (12)$$

where

q_e = Equilibrium adsorbent-phase concentration of adsorbate (mg g^{-1})

q_m = Theoretical saturation capacity (mg g^{-1})

K = Activity coefficient related to mean free energy of adsorption ($\text{mol}^2 \text{KJ}^{-2}$)

ε = Polanyi potential (KJ mol^{-1})

The model is summarized by two basic parameters: the maximum adsorption capacity (Q_m) and the characteristic energy of adsorption (ε) [86]. Two parameters describe adsorption equilibria, which are often utilized in solid-liquid interfaces.

ε is related to the energy required to transfer one mole of the adsorbate from infinity to the adsorbent surface. It is calculated as:

$$\varepsilon = \frac{1}{\sqrt{2k}} \quad (13)$$

If $E < 8 \text{ KJ/mol}$, the adsorption is physisorption.

If $E > 8 \text{ KJ/mol}$, the adsorption is chemisorption.

3.5 Kinetics model

3.5.1 Pseudo-first order

The direct correlation between the adsorption rate and the difference between the equilibrium adsorption capacity (q_e) and the adsorption capacity at a particular time (q_t) forms the foundation of the pseudo-first-order model, as defined by the Lagergren equation. This is the usual way to represent the model.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (14)$$

where q_e and q_t = the amount of chromium adsorbed on the adsorbent at equilibrium, and at any time t , respectively, and K_f = the Rate constant.

The slopes and intercepts of the $\log(q_e - q_t)$ vs. $t(\text{min})$ plot are shown in Fig. 17. The first-order rate constant K_f was calculated to be $0.034453/\text{min}$, and the equilibrium adsorption capacity was 106.23 mg/g .

3.5.2 Pseudo-second order

The pseudo-second-order model assumes that the adsorption rate is proportional to the square of the difference between q_t and q_e . The model is expressed as.

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (15)$$

where K_f = Equilibrium rate constant, and q_e and q_t are the amounts of chromium adsorbed on the adsorbent at equilibrium and time t , respectively.

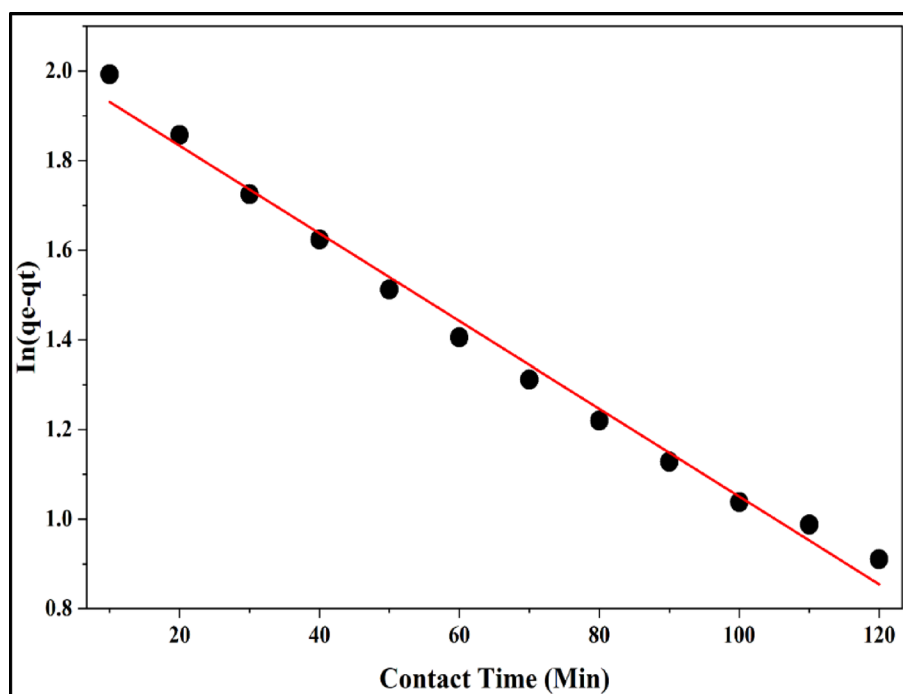


Fig. 17 Pseudo-first-order kinetics for Cr(VI) removal using BRSP

The slopes and intercepts of the t/q_t versus t (min) plot are presented in Fig. 18. The pseudo-second-order rate constant K_2 was calculated as 5.35×10^{-4} g/mg/min and q_e as 105.6073 mg/g, respectively.

Kinetic studies on Cr(VI) adsorption revealed that the adsorption process was well-fitted by pseudo-first-order and pseudo-second-order kinetics, as shown in Fig. 13. The pseudo-first-order model produced an equilibrium adsorption capacity of 106.83 mg/g, with a rate constant of $0.034453 \text{ min}^{-1}$. The pseudo-second-order model yielded a capacity of 50.6073 mg/g and a rate constant of 5.35×10^{-4} g/mg/min, as shown in Table 6. The fact that the data were best fitted to the pseudo-second-order model indicates that the adsorption mechanism was chemical adsorption involving valence forces or electron sharing [87]. This is an essential revelation of adsorption kinetics and adsorbent selection processes to achieve improved efficiency of Cr(VI) removal by adsorbents. As we see in Fig. 12, the kinetic data confirm this mechanism, with the pseudo-second-order model showing the best fit only. This suggests that chemisorption is the main rate-controlling step, where electrons are shared between Cr(VI) and the active groups of the adsorbent. This further shows that the adsorption rate depends mainly on the availability of binding sites rather than the concentration of the solute. The Langmuir and PSO models further confirm that BRSP removes Cr(VI) through chemical bonding on a single-layer surface. This process shows strong specific interactions, making BRSP an effective material for chromium removal.

3.6 Thermodynamics study

Thermodynamic parameters are crucial for understanding the feasibility, nature, and mechanisms of adsorption processes. The main thermodynamic parameters were used to evaluate the Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0), and the entropy change. (ΔS^0) [88], which provides insight into whether the adsorption process

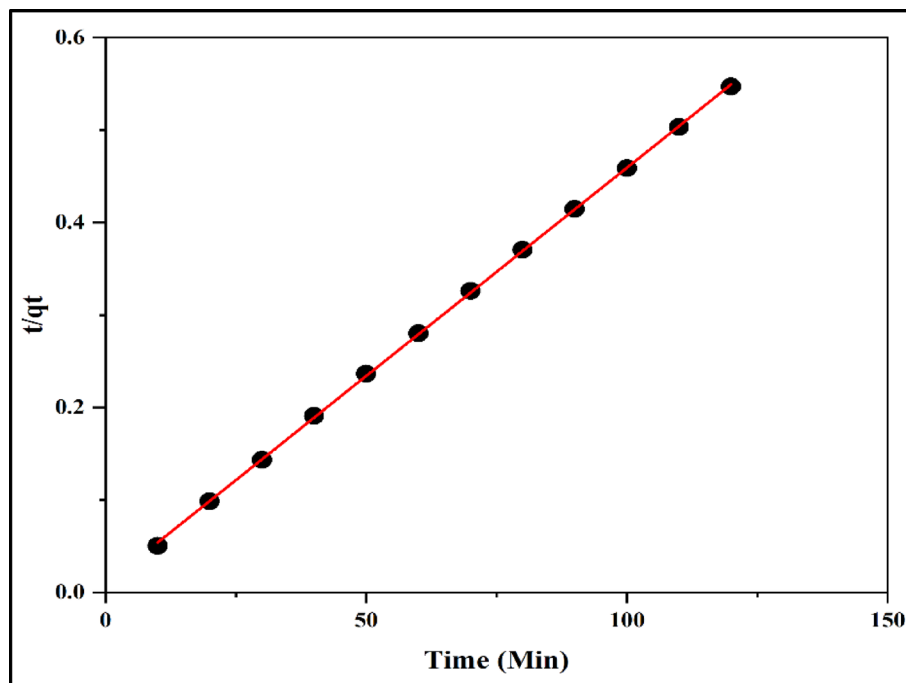


Fig. 18 Pseudo-first-order kinetics for Cr(VI) removal using BRSP

Table 6 Kinetic Parameters for Cr(VI) adsorption onto Sawdust

Kinetics	Parameter	Value
Pseudo-first order	q_e	106.23 mg/g
	K_1	0.0344/min
	R^2	0.99757
Pseudo-second order	q_e	105.60729 mg/g
	K_2	5.35×10^{-4} g/mg/min
	R^2	0.99998

is spontaneous, exothermic or endothermic, and the degree of randomness at the solid–liquid interface [89].

Calculation of thermodynamic parameters.

The standard Gibbs free energy change (ΔG) for adsorption was calculated using the following equation:

$$\Delta G^0 = -RT \ln K_C \quad (16)$$

where.

R = Universal gas constant (8.314 J/mol^{-1}).

T = Temperature (K).

K_c = Equilibrium constant of the adsorption process.

The equilibrium constant K_c is calculated from.

$$k_C = \frac{C_{ads}}{C_e} \quad (17)$$

where

C_{ads} = Concentration of adsorbate on the adsorbent at equilibrium (mg/L).

C_e = Equilibrium concentration of the adsorbate in solution (mg/L).

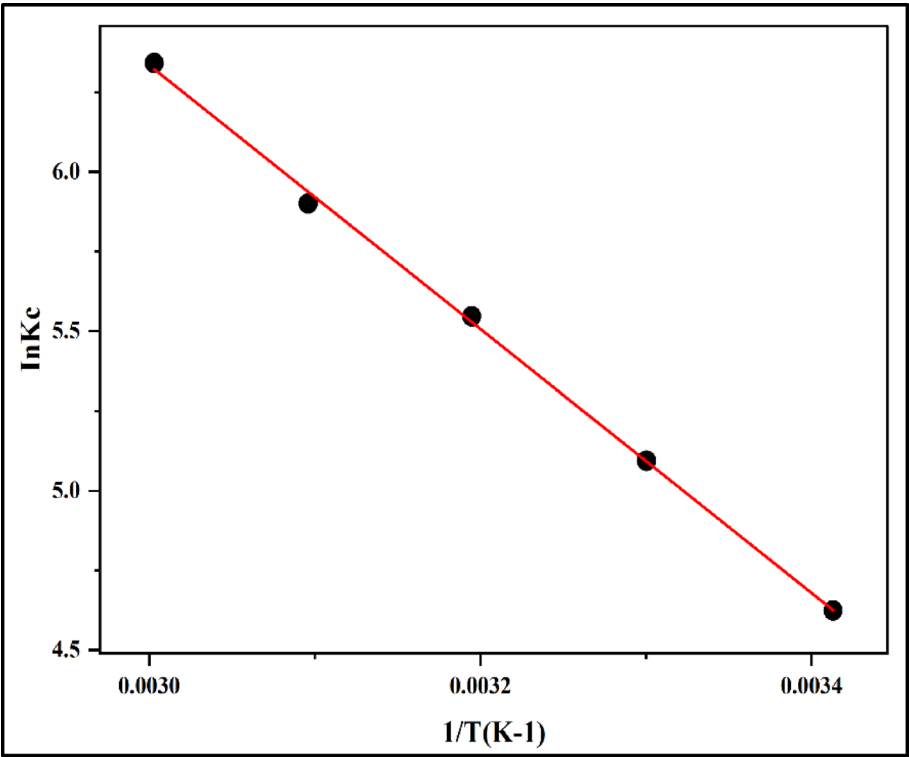


Fig. 19 Vant Hoff plot for the removal of Cr(VI) by adsorption using BRSP

Table 7 Thermodynamics interpretation

Temperature (°C)	ΔG (kJ/mol)	ΔH° (KJ/mol)	ΔS° (kJ·mol ⁻¹)	R ²
20	− 1.0764	34.4198	1.774811	0.99884
30	− 1.18112		1.186698	
40	− 1.29107		0.892773	
50	− 1.40607		0.716518	
60	− 1.45289		0.597879	

The energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were evaluated for each sample.

The Van't Hoff equation was used.

$$\ln k_C = \frac{-\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R} \tag{18}$$

By plotting van 't Hoff $\ln K_c$ vs. $1/T$, the slope ($-\Delta H^0 / R$) and intercept ($\Delta S^0 / R$) can be determined, as shown in Fig. 19. The results are presented in Table 7.

Table 7 presents the thermodynamic properties of the adsorption process, indicating the feasibility and nature of the adsorption. The negative ΔG values at all temperatures suggest that adsorption was spontaneous. The endothermic nature of adsorption (positive $\Delta H^0 = 34.4198 \text{ kJ}\cdot\text{mol}^{-1}$) indicates preferential adsorption at higher temperatures. A positive ΔS^0 indicates a higher disorder at the solid–liquid interface upon absorption. The high R^2 value ($R^2 = 0.99884$) of the van't Hoff plot demonstrates a strong linear correlation between the curve endpoints, supporting the accuracy of this thermodynamic study.

Table 8 Comparative optimized conditions and adsorption capacities of various biomass-based adsorbents for heavy metal removal

Biomass	Metal	pH	Contact time (min)	Adsorption capacity (mg/g)	Reference
<i>Cordia africana</i>	Pb (II)	7	50	178.19	[90]
<i>Cordia africana</i>	Ni (II)	7	70	104.45	
<i>Manilkara</i> spp	Pb (II)	5	70	145.04	[95]
Neem leaf powder	Cd (II)	9.5	300	158	[92]
<i>Dalbergia sissoo</i> sawdust	Cd (II)	6.7	80	147.05	[96]
<i>Alstonia Macrophylla</i> Saw Dust	Pb (II)	7.5	600	204	[91]
Wheat bran	Pb (II)	6	60	86.96	[94]
<i>Eucalyptus Camaldulensi</i>	Cr(VI)	10	120	47.619	[93]
BRSP	Cr(VI)	4	60	106.86	This study

4 Comparative discussion of adsorption performance with literature reports

The comparative adsorption results presented in Table 8 show the critical role of biomass type, chemical modification, and operational parameters in influencing the adsorption process. Among the reported biomasses, Pb(II) removal by *Cordia africana* and *Alstonia macrophylla* has reached the highest points of 178.19 mg/g and 204 mg/g [90, 91] respectively, at around neutral pH, while *Manilkara* spp. (145.04 mg/g) at pH 5 worked efficiently. Neem leaf powder was extremely effective (158 mg/g) in alkaline media (pH 9.5) [92], while the chemically treated *Dalbergia sissoo* sawdust was recorded at 147.05 mg/g for Cd(II) at pH 6.7, confirming the positive impact of surface modification. *Eucalyptus camaldulensis* and wheat bran, however, exhibited only moderate adsorption capacities (47.62 mg/g and 86.96 mg/g, respectively) [93, 94]. However, their low prices and availability still make them suitable for large-scale use as adsorbents. These results collectively reveal that the adsorption mechanism is governed by a synergistic contribution of electrostatic attraction, ion-exchange, and complexation with surface functional groups, all of which are strongly modulated by pH. Importantly, the adsorption performance of BRSP represents a sustainable balance between raw biomass and highly engineered sorbents, offering high efficiency without the need for intensive chemical modification. This underlines its promise as an economically viable and environmentally friendly adsorbent for heavy metal remediation in real wastewater applications.

B. racemosa sawdust powder (BRSP) exhibited a relatively comparable adsorption capacity of 106.86 mg g⁻¹ at pH 4, similar to other biomass reported below.

5 Conclusions

The present research concludes that *Bauhinia racemosa* sawdust powder (BRSP) is an efficient material for adsorbing Cr(VI) from aqueous solutions. Material characterization demonstrated a heterogeneous surface covered with active functional groups like hydroxyl, carboxyl, amine, and aromatic moieties that are responsible for the high metal ion affinity and high specific surface area. The adsorption process was found to be extremely pH-dependent, and the optimum performance was seen at pH 4.0.

Batch experiments showed that particle size, initial concentration of Cr(VI), and dosage of adsorbent had significant effects on the efficiency of biosorption. Maximum removal was obtained with the smallest particle size (75 microns), the lowest initial concentration (100 mg/L), and the optimal biomass dosage (0.5 g). Kinetic modeling reveals

that chemisorption is the prevailing mechanism, which is best fitted by the pseudo-second-order model. Isotherm studies follow the Langmuir model, reflecting monolayer adsorption with an adsorption capacity of 106.86 mg/g. Thermodynamic results indicated that the biosorption process was spontaneous and endothermic. FTIR and SEM-EDX analysis confirm the binding of Cr(VI) and modification of surface morphology and elemental constitution after adsorption.

These results position BRSP as a low-cost, sustainable, and high-capacity biosorbent, providing an environmentally friendly approach to industrial wastewater treatment. The combined kinetic, thermodynamic, and mechanistic studies provide insights into Cr(VI) biosorption, emphasizing the effectiveness of BRSP in comparison to other biomasses.

5.1 Limitations and future perspective

This study suggests that *Bauhinia racemosa* sawdust, a low-cost biosorbent, exhibits substantial efficiency in removing Cr(VI); however, it was carried out under controlled batch conditions, which may not fully represent real wastewater complexity and the influence of competing ions, pH, and other factors. Future research should encompass continuous fixed-bed systems, multicomponent adsorption, and advanced surface characterization method to obtain deeper understanding. Pilot-scale studies, computational modeling, and techno-economic evaluation are recommended to establish the process scalability.

Abbreviations

AC	Ash content
ADWG	Australian drinking water guidelines
APHA	American public health association
AR	Analytical reagent
ASTM	American society for testing and materials
AT	Temkin binding equilibrium constant
BELSORP	Brunauer–Emmett–Lifshitz sorption analyzer (Instrument for BET surface area analysis)
BET	Brunauer–Emmett–Teller
BIS	Bureau of Indian standards
BIT28 / BIT36	Bio-tech instrument models (hot air oven / muffle furnace)
BRSP	<i>Bauhinia racemosa</i> sawdust powder
BT / BTI	2008 / BTI–29–bio–technics instrument models
CB	104–chem biotech UV–Vis spectrophotometer (Model)
CPCB	Central pollution control board (India)
Cr(VI)	Hexavalent chromium
DAS	Data availability statement
DPC	1,5–Diphenylcarbazine (Colorimetric Reagent)
EDS / EDX	Energy–dispersive X–ray spectroscopy
EQ618	Equitrans digital pH Meter (Model)
EU	European union
FC	Fixed carbon
FTIR	Fourier transform infrared spectroscopy
HNO ₂	Nitric acid
ID	Identification
IR	Infrared
ISO	International organization for standardization
JWWA	Japan water works association
J / KJ ²	Kilojoule / Kilojoule squared
K _L	Langmuir adsorption constant
K _T	Temkin isotherm equilibrium constant
MC	Moisture content
MOH	Ministry of health (Malaysia)
NH	Amine group
OH	Hydroxyl group
PSO	Pseudo–second–order (kinetic model)
pHPZC / PZC	Point of zero charge
RL	Dimensionless separation factor (Langmuir)
SANS	South African national standard
SBET	Specific surface area (from BET analysis)

SEM / SEM	EDX–scanning electron microscopy / energy dispersive X–ray spectroscopy
USEPA	United States environmental protection agency
UV	Ultraviolet
VM	Volatile matter
WHO	World Health Organization

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Author contributions

1st author Experimentation and analysis for a research study, Collected data, worked on data and analysis, tools, and wrote all manuscript sections. 2nd author Supervision conceived and planned the study, reviewed and corrected the manuscript.

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Data availability

Data available on request from the authors.

Declarations

Ethics approval and consent to participate

Not Applicable.

Consent form for publication

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Competing interests

The authors declare no competing interests.

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